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ABSTRACT

This booklet contains three separate papers suitable for use in an advanced high school or college chemistry course. The first paper provides background information on acids and bases. The second paper provides additional background information, focusing on certain aspects of atmospheric chemistry as it relates to the acid rain problem. An attempt was made to keep the material as simple as possible and to provide enough vocabulary to understand the arguments of the experts but not to overwhelm the student with the chemical details of the process. The third paper, which focuses on the acid rain controversy, consists of a number of exercises in a self-instructional format. The paper can be used either as a classroom activity in which students respond to the questions or as a model from which teachers can develop their own material either on acid rain or some other topic of interest. Several suggestions are offered if teachers decide to use the exercises in a classroom setting. In addition, a list of discussion questions to extend various exercises and questions posed in the textual material are included. (JN)

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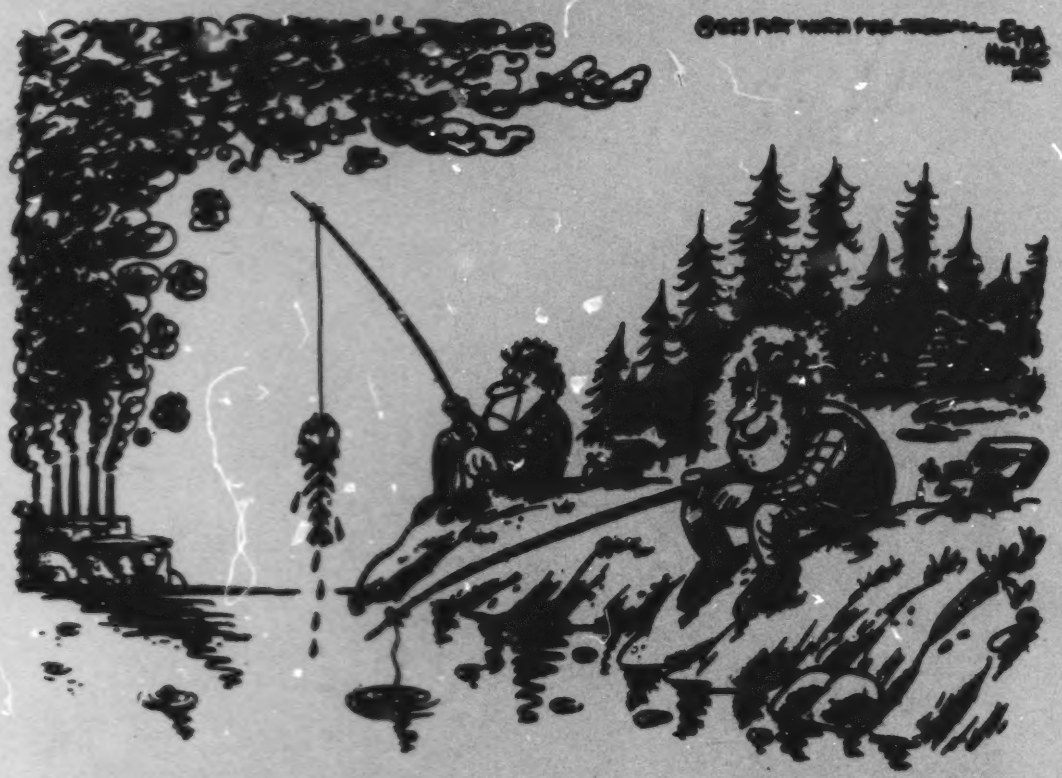
ACID RAIN

MATERIALS FOR CLASSROOM USE



"They always bite better after a good rain — what makes you think that was acid rain?"

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by LANCE FACTOR and ROBERT G. KOOSER

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Acknowledgments

This booklet contains three separate papers suitable for use in an advanced high school chemistry course or a college chemistry course. Each paper is numbered separately, and the authors offer suggestions on how each may be used in their "Note To Teachers".

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Any opinions, findings, conclusions, or recommendations expressed herein are those of the authors and do not necessarily reflect the views of the National Science Foundation or the National Endowment for the Humanities.

A NOTE TO TEACHERS

In this short note to teachers we wish to describe our aims and suggest several ways this material may be used in a chemistry classroom.

Our concern is that in teaching chemical facts to students in introductory courses certain aspects of the use and application of chemical knowledge, though relevant, are not easily addressed. For instance, a topic such as acid rain carries with it a host of complex economic and political questions which cannot be addressed in limited classroom time. We do not raise any of these questions in our material on acid rain. However, we do bring up some of the fundamental questions about applied science and the way it influences the acid rain debate. First because it is widely acknowledged that there is no complete understanding of the nature and scope of the acid rain problem, it is easy to disabuse the student of the belief that science always has the "right answers". Secondly, because there is uncertainty, experts disagree. The fact that scientists frequently generate conflicting opinion on current topics of public interest is often hidden from students because textbooks either omit all controversial topics or present them in the same factual way as incontrovertible subjects like the law of multiple proportions. In our opinion both alternatives subtract from an adequate understanding of the relationship between science and society. By omitting controversy, textbooks fail to demonstrate how basic scientific knowledge can be useful in facing current issues and by presenting truncated opinions as if they had scientific concensus, textbooks contribute to the dangerously one-sided view that science is monolithic, value-free and authoritative. The irony, of course, is that every textbook writer will preface his new edition of basic chemistry with the avowed purpose of creating an informed laity or improving scientific literacy. These are noble aims which, in our opinion, cannot be achieved without showing how and why experts disagree. Our material on acid rain can correct these misconceptions because they face up to the fact that experts disagree and that experts mix factual information with evaluative or interpretive conclusions. Our material allows the student to analyze the nature and reasoning of both sides of the acid rain debate. It attempts to make them more sensitive to the ways in which testimony of fact is mixed with testimony of inference. It brings out the underlying logical form of the debate through a series of questions which allow the student to use his or her knowledge of chemistry to identify certain deficiencies in the debate.

There are two parts--one on background material and one on the acid rain controversy. The background material again has two parts. The first part is a very simple introduction to acids and bases which will be useful if one has not yet touched on

acid-base theory. It provides appropriate background information in a general science class where such material might not ordinarily be covered. Certainly, students who have had a traditional unit on acids and bases will not need to use this section except for review. The second part of the background material covers certain aspects of atmospheric chemistry as it relates to the acid rain problem. An attempt was made to keep the material as simple as possible and to provide enough vocabulary to understand the arguments of the experts but not to overwhelm the student with the chemical details of the processes.

The second section, entitled "The Acid Rain Controversy", is presented in a self-instructional format, all or part of which could be considered as exercises to hand in. The teacher may use this section in two general ways; as a classroom exercise in which the students would respond to the questions or as a model from which the teacher could develop his or her own material either on acid rain or some other topic of interest.

If the study is used in the classroom, again several formats are possible. After a review of the background material, the students could be given the second section and asked to respond to the questions on their own. This could be followed by the class as a whole discussing various aspects of the acid rain controversy. The exercises in the study are particularly worthy of discussion. For instance, Exercise 1, which asks students to rate various statements for their factual content, would be a good place to ask questions about the student's reasons for ranking and how we can tell the difference between rational criticism and polemic statements. Another possibility is to work through the case study with the entire class responding reserving the final exercise as an individual project. We believe the acid rain segment of a chemistry course will take no more than two class periods. We have included a list of discussion questions to extend various exercises and questions posed in the text.

As has been suggested, we hope our work may serve as a model for further inquiries into value-laden disagreements. Possibly, the emerging dioxin controversy will be as suitable as acid rain to convey the complexities of chemical systems outside the laboratory. The debate shows expert disagreement and value conflict.

Those who are interested in further reading on the educational objectives behind this approach may consult Robert Kooser and Lance Factor, "Does Chemistry Really Work This Way?" in the Journal of Chemical Education, volume 59, December 1982, page 1010.

Discussion Questions

Here are some possible questions which could be used with the section on acid rain. The numbers refer to the question numbers in the text.

Exercise 1. What were your reasons for ranking the statements the way you did? How do we tell a reasoned statement from one with emotional or nonsubstantive content? Could these reasons be useful in analyzing other statements by scientists that appear in the press?

Question 3. In arguments like EPRI's, how important is it to select the evidence? Does this make the argument scientific or nonscientific?

Questions 16-18. Here the whole issue of how what one is trying to prove can influence the nature of the arguments used and the facts that are selected is raised. It would be appropriate to ask whether a case like acid rain is in any way different from a more scientific controversy, say like the safety of aspirin or the carcinogenic nature of sacchrin.

Exercise 2. What criteria did you use to decide the categories into which you placed the arguments? How would the EPRI respond to assertions like (2) and (6)? Are there other bits of evidence that environmentalists might cite?

As a class exercise, the teacher might divide the class into two parts, one representing the power companies and the other the environmentalists. The two sides would then be asked to respond from their assigned point of view to selected questions in a debate format. In that regard, the short bibliography at the end of this section might be useful for further background reading.

Questions 21-23. The facts that are presented above these questions could be used in a discussion about the validity of the conclusion that the cause of lake acidification in North America is acid rain from industrial pollution. The strength of the argument might be compared to some of the conclusions drawn by the power companies.

Exercise 3. This is a chance for the student to draw his or her own position from the limited arguments presented in the text. It might be expected that different students will come to different positions and this would be an excellent opportunity to have a general discussion about individual student perceptions of the issue. This exercise also raises a difficult pedagogical problem: How much must to be known about a problem before an informed decision can be made?

Bibliography

This is a short bibliography of further readings in the acid rain controversy. It is not comprehensive nor does it deal at all with very extensive technical literature on the subject. The readings are mostly summaries and are directed toward the lay-person.

General Review of the Literature

Cowling, E. B., "Acid Precipitation in Historical Perspective", Environmental Science & Technology, vol. 16, no. 2, 1982, pp. 110-ff. This is a rather complete review of the literature including most of the important technical papers and contains an extensive bibliography.

General Reviews of the Acid Rain Problem

Report by the Comptroller General of the United States, "The Debate Over Acid Precipitation--Opposing Views--Status of Research", Sept. 1982. Single copies can be gotten for $3.25 U.S. G.A.O. Document Handling, P.O. Box 6015, Gaithersburg, MD, 20760. This report summarizes the status of knowledge about acid rain up to the publication date. It has a rather evenhanded treatment of the state of knowledge.

Ember, L. R., "Acid Pollutants: Hitchhikers Ride the Wind", Chemical & Engineering News, Sept. 14, 1981, pp. 20-ff. Besides being a fairly complete summary of the problem, this article points out the disagreements among experts and points to several areas where more work is needed.

Gibbons, D. L., "Acidic Confusion Reigns", Sciquest, January, 1982, pp. 10-16. This is a general review easily read by a layperson.

Likens, G. E., R. F. Wright, J. N. Galloway and T. J. Butler, "Acid Rain", Scientific American, October, 1979, pp. 43-51. A general review by one of the leading environmental researchers in the field of acid rain.

Papers Outlining the EPRI's Position

Goodman, C. H., "Acid Rain Presentation", Energy Conference, Citizens Advisor Council on Energy, Athens, Georgia, Nov. 1982.

Jansen, J. J., "Acid Precipitation-A Review of the Issues and its Uncertainties", Dec. 1979, unpublished paper.

Harrison, W. B., "Economics and Acid Deposition", Southeast Conference on Acid Deposition, Atlanta, Georgia, June, 1982.

Papers Outlining the Environmentalist's Case

Cowling, E. B. and R. A. Linthurst, "The Acid Precipitation Phenomenon and its Ecological Consequences", Bioscience, vol. 31, no. 9, 1981, pp. 649-654.

Howard, R. and M. Perley, Acid Rain: The Devastating Impact on North America, McGraw-Hill, New York, 1982, ISBN 0-07-030546-3.

Likens, G. E., "Acid Precipitation", Chemical & Engineering News, Nov. 22, 1976, pp. 29-44.

Subcommittee on Acid Rain of the Standing Committee on Fisheries and Forestry, Still Waters: The Chilling Reality of Acid Rain, Minister of Supply and Services, Canadian Government, Ottawa, Canada, 1981. Bibliography.

Background Information: Acids and Bases

Water. It's everywhere. It is the stuff of life. Since our ecosystem depends so much on water and its properties, we are going to investigate certain chemical facts about water and some compounds that dissolve in water. These chemical facts will help us understand some of the technical issues in the acid rain case study to follow. In addition, you will learn some atmospheric chemistry.

Acids and Bases:

Water has an interesting property which scientists call <u>autoionization</u> and is expressed in simple terms by reaction (1);

$$H_2O \rightleftharpoons H^+ + OH^- \qquad (1)$$

In pure water, there are, of course, equal amounts of H^+*, hydrogen ion, and OH^-, the hydroxide ion. Such a solution is said to be a <u>neutral</u> solution.

Many substances, when added to water, dissolve and upset the balance between the hydrogen and hydroxide ions. Substances which create an excess of hydrogen ions over hydroxide ions are called <u>acids</u>, while those that create an excess of hydroxide are called <u>bases</u>. Table I lists some common acids and bases found in the home. To see how these substances can create an excess, the following reactions show the source of the H^+ or OH^-.

vinegar (acetic acid) $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$ (2a)

lye $KOH \longrightarrow K^+ + OH^-$ (2b)

ammonia $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$ (2c)

Remember, that the reaction (1) is an equilibrium and this causes a chemical constraint on the autoionization reaction, namely that product of the concentration of the hydrogen and hydroxide ion concentrations must be constant.

$$K_w = [H^+]\,[OH^-] \qquad (3)$$

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*While we will be using "H^+" to represent the hydrogen ion, it is more correct to write it as H_3O^+. The bare proton does not exist by itself in solution, rather it is associated with a number of water molecules.

This constant has a value of 1×10^{-14} at 25° C. This means if the hydrogen ion concentration goes up as a result of the addition of an acid to the water, the hydroxide concentration must go down so that their product is constant. For instance, if the hydrogen ion concentration becomes 1×10^{-3}M, then

$$[OH^-] = 1 \times 10^{-14}/1 \times 10^{-3} = 1 \times 10^{-11}M \qquad (4)$$

Compare this to the concentrations in pure water. In pure water, the hydroxide and hydrogen concentrations must be the same since for every water molecule that dissocates, one hydroxide and one hydrogen ion are produced. Hence $[H^+] = [OH^-]$ or $(H^+)^2 = 1 \times 10^{-14}$. Taking the square root one has $[H^+] = [OH^-] = 1 \times 10^{-7}$M (where 'M' stands for the concentration unit, molarity).

Solutions where hydrogen ion predominate over hydroxide ion are said to <u>acidic</u>. These will have hydrogen ion concentrations greater than 1×10^{-7}M. Solutions where the hydroxide ion concentration is greater than hydrogen ion concentration are said to be basic and here the hydrogen ion concentration is less than 1×10^{-7}M.

The pH Scale

The hydrogen ion concentration is a measure of the acidity of a particular solution. The hydrogen ion concentration in typical solutions can vary from about 1 M (very acidic) to about 1×10^{-14}M (very basic). This is a very large range of variation, so to make reference to the acidity of a solution somewhat less cumbersome, a Swedish chemist, Sorensen, suggested that scientists use what is now called the <u>pH scale</u>. pH is defined as

$$pH = - \log [H^+]^* \qquad (5)$$

Because of the mathematic properties of the logaritamic relation, the pH scale varies typically from 0 ($H^+ = 1M$) to about 14 ($H^+ = 1x10^{-14}M$). Notice in pure water $[H^+] = 1 \times 10^{-7}$ so $pH = - \log (1x10^{-7}) = 7$. Thus when the pH=7, the solution is said to be <u>neutral</u>. pH's less than 7 are acidic while pH's greater than 7 are basic. Table II shows some correlations among, H^+, OH^- and pH. Notice the important relationship that as the H^+ concentration gets larger (more acidic), the pH gets <u>smaller</u>. Also listed in Table II are the approximate pH's of some common fluids to give you an idea about the range of pH values found in the everyday environment.

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*The advent of the electronic calculator with function keys for logarithms has made calculations using them much easier. The point you should remember is that the property of the log function is such that the variation by a factor of ten in the argument of the log (the hydrogen ion concentration) causes only a change of 1 in the log itself.

Neutralization

Acids and bases have been defined, now you will explore some of their properties which are important in the understanding of acid rain. One of the most important and obvious properties of acids and bases is their reactivity toward each other. It has been known for centuries that an acid plus a base yields a salt plus water. The process whereby an acid and a base react together is called neutralization, although in many instances the result is not a neutral solution in terms of pH. Some examples of neutralization reactions are given here.

$$NaOH + HCl \longrightarrow H_2O + NaCl$$

$$HNO_3 + KOH \longrightarrow H_2O + KNO_3$$

While the salt plus water generalization for most acid-base reactions holds true, it does not always describe all acid-base reactions. For instance, when the base ammonia reaction with an acid, say HCl for example, the result it:

$$NH_3 + HCl \longrightarrow NH_4Cl$$

No water is created in this reaction.

Strong and Weak Acids and Bases

Chemists classify acids and bases into two categories, strong and weak. A strong acid or base is defined as a compound when dissolved in water yields as many moles of H^+ or OH^- as moles of compound originally placed in water. Another way to say the same thing is that this dissociation (coming apart of the compound) is complete. Some examples are:

$$HCl \longrightarrow H^+ + Cl^- \qquad (6a)$$

$$NaOH \longrightarrow Na^+ + OH^- \qquad (6b)$$

You should note that the terms 'strong' and 'weak' refer to the degree of dissociation of the acid or base and not to the concentration, hence it is not a contradiction to talk about a dilute solution of a strong acid. There are only a few strong acids and bases. Some of the more common ones are listed in Table III. Two of those, sulfuric and nitric, play a major role in the acid rain problem.

As a corollary to the strong case, there are a large number of substances that chemists classify as weak acids or bases. These are compounds that do not completely dissociate in solution, hence there may be appreciable concentrations of the parent molecule present, counter to the strong case where very little to none remains. Two of the most common examples are given in equations 2a and 2c, acetic acid and ammonia. Notice that the two sides of the equation are connected by double arrow.

This is to emphasize the fact that there is a dynamic interchange or equilibrium going on which means that any given molecule will associate, disassociate and reassociate continually but on the average there is a constant number of associated and disassociated molecules.

Not all weak acids or bases dissociate to the same degree. Table IV lists several common weak acids and shows the hydrogen ion concentration for solutions of equal concentration of the parent acid, thus we see there are degrees of 'weakness'. In addition, there are several weak acids that are capable of giving up more than one hydrogen ion. An example that is important in the chemistry of rain is carbonic acid, H_2CO_3* which can undergo the following steps:

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \qquad (7a)$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^= \qquad (7b)$$

HCO_3^- is known as the bicarbonate ion and is farmiliar as the negative ion in baking soda, $NaHCO_3$. $CO_3^=$ is called the carbonate ion; as the sodium salt, Na_2CO_3, sodium carbonate is used in laundry formulations and as 'washing soda'.

Ammonia, NH_3, is the most common weak base (see equation 2c). You should notice that the negative ion that is derived from the dissociation of any weak acid is itself capable of taking on a hydrogen ion to form the undissociated acid. For instance, if you dissolve washing soda in water, it dissociates into $2Na^+$ and $CO_3^=$. The carbonate ion will then undergo the following reaction:

$$CO_3^= + H_2O \rightleftharpoons HCO_3^- + OH^- \qquad (8)$$

thus creating an excess of hydroxide ion over hydrogen ion and making a basic solution. In other words, when a weak acid dissociates, it forms, on reacting, a weak base. This is called the conjugate base ($CO_3^=$) of the weak acid HCO_3^-. Similarly in the ammonia case the weak base NH_3 has the conjugate weak acid the ammonnium ion, NH_4^+. In equation 2c, you see the weak base ammonia which reacts to form the ammonium ion, NH_4^+. Now should an ammonium salt like ammonium nitrate, NH_4NO_3--a common fertilizer--dissolve in water, then this reaction would occur:

$$NH_4^+ \rightleftharpoons NH_3 + H^+ \qquad (9)$$

creating an excess of hydrogen ions and an acidic solution. Another example might suffice here. Acetic acid, CH_3COOH, the

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*H_2CO_3 is somewhat of a convenient misnomer. Carbonic acid is formed when carbon dioxide, CO_2, dissolves in water. However, not all the dissolved CO_2 combines with a water molecule to make the acid, some remains as molecular CO_2. "H_2CO_3" refers to both CO_2 and that which combines with water for form H_2CO_3.

major acidic component of vinegar is a weak acid, thus a solution of a salt of the acid, sodium acetate (in solution it will give Na^+ and the acetate ion, CH_3COO^-) will be basic because of the presence of the conjugate base of acetic acid, the acetate ion. You should notice that the positive and negative ions derived from strong acids and bases have themselves no acid or base properties and are called neutral. Some examples are $Cl^-(HCl)$, NO_3^- (HNO_3), $Na^+(NaOH)$ and $Ca^{+2}(Ca(OH)_2)$.

Buffer Solutions

Of great importance in nearly all biological systems are particular solutions of acids and bases that are called buffer solutions. Webster's International Dictionary defines 'buffer' as "any of various devices, apparatus, or pieces of material designed primarily to reduce shock due to contact" and in a chemical way, this is what a buffer solution does. It behaves in such a way that additions of acid or base to the buffer solution will result in only small changes in the pH of the solution from its original value.

What does it take to make a buffer solution? There must be present both a weak acid and its conjugate base salt in significant amounts. In laboratory situations, buffers are usually made by mixing a solution containing a weak acid and its negative ion in the form of a salt. Thus, a solution of acetic acid (vinegar) and sodium acetate ($NaCOOCH_3$) would form a buffer solution.

While you will not be concerned with details of buffer solutions, it will be useful to think a little bit about how they work. In a buffer solution the pH is established based on two factors, the degree of dissociation of the weak acid (that is fixed by the type of acid used) and the ratio of the concentrations of weak acid to its negative ion; e.g. (CH_3COOH) / (CH_3COO^-) in the case in the paragraph above. If some base is added to the acetate buffer, the acetic acid will react with it as follows:

$$CH_3COOH + NaOH \longrightarrow CH_3COO^- + Na^+ + H_2O \qquad (10)$$

(Water is made by the union of the H^+ from the acid and the OH^- from the base). Notice that the amount of acetic acid present will decrease and the amount of the acetate, the anion, will increase. The ratio of acid to conjugate base changes so there is some pH shift, but the effect is much less than in the absence of conjugate pair. Calculations show that if in the original concentrations of the acetic acid and the acetate ion are both .1 M that in a liter of solution with 1 gram of NaOH in it, the pH would change from about 4.5 to 4.8. If same amount of NaOH were placed into pure water the pH would change from 7 to about 12.4. Clearly, a buffer solution has the capacity to "reduce the shock' from contact with acids and bases.

The ability of a buffer solution to absorb the shock from contact with acids and bases is not limitless. As more acid or base is added, the substances which create the buffering effect are used up. There comes a limit when the addition of more acid or base can not be countered. Thus every buffer solution has its limits in terms of its buffering capacity. The buffering capacity is determined mainly by the initial concentrations of the weak acid and its basic salt. The phenomenon will become important later when we discuss acid rain and natural waters.

Buffers are extremely important in biological and ecological situations. Most living systems require a very narrow range of pH values in order to function normally. For instance, human blood contains buffers which fix the pH at about 7.4. Should the pH of the blood fall outside the range from 7.0 to 7.8, as might happen from certain kinds of diseases, death might occur. The same is true for aquatic life in natural waters. It has been demonstrated in the laboratory that if the pH of the water in which fish are living becomes too acidic, fish fry fail to develop normally and reproduction of adult fish is interrupted. Another example of a natural buffer is the carbonate system. The workings of this system are shown in Figure 1. It should be emphasized that this is only one of several possible buffering actions that take place in natural waters. Many compounds are dissolved in waters and many can contribute to the overall buffering action. Limestone is sparing soluble in water (in fact it is the cause of water hardness in many areas) and is a source of carbonate ion. Carbon dioxide in the atmosphere, mainly from the combustion of fuels and respiration of animals, and plants dissolves in the water forming carbonic acid. Bicarbonate ion from the dissolved limestone and the carbonic acid formed from carbon dioxide in air make up a natural buffering system.

TABLE I

Common Acids and Bases

Compound	Formula	Uses
Acids		
Acetic acid solution (vinegar)	CH_3COOH	Pickling, seasoning
Hydrochloric acid	HCl	Cleaning masonary
Sulfuric acid	H_2SO_4	Drain cleaner, battery acid
Citric acid	$HOOC(OH)C(CH_2COOH)_2$	Active ingredient in fruit antibrowning agents, present in citrus fruits
Boric acid	H_3BO_3	First aid, eye wash solutions
Hydrogen peroxide	H_2O_2	Hair bleach, antiseptic
Oxalic acid	HOOCCOOH	Present in spinach, rhubarb
Phosphoric acid	H_3PO_4	Present in some soft drinks like colas
Potassium bitartarate (Cream of tartar)	$KOOC(CHOH)_2COOH$	Baking powder
Carbonic acid	H_2CO_3	Fizzing agent in soft drinks
Bases		
Ammonia	NH_3	Cleaning agent
Sodium hypochlorite	NaOCl	Active ingredient in bleaches
Potassium hydroxide	KOH	Drain cleaner
Calcium hydroxide (slaked lime)	$Ca(OH)_2$	Antacid
Magnesium hydroxide (Milk of magnesia)	$Mg(OH)_2$	Laxative
Calcium carbonate	$Ca(CO_3)$	Limestone

TABLE II

Relationship among pH, H^+ and OH^- in Water

	pH	$[H^+]$	$[OH^-]$
Battery Acid	1	.1	1×10^{-13}
Lemon juice	2	.01	1×10^{-12}
Vinegar	3	.001	1×10^{-11}
	4	1×10^{-4}	1×10^{-10}
	5	1×10^{-5}	1×10^{-9}
	6	1×10^{-6}	1×10^{-8}
Milk	7	1×10^{-7}	1×10^{-7}
Human Blood	8	1×10^{-8}	1×10^{-6}
Sea Water	9	1×10^{-9}	1×10^{-5}
	10	1×10^{-10}	1×10^{-4}
	11	1×10^{-11}	.001
Ammonia	12	1×10^{-12}	.01
Lye	13	1×10^{-13}	.1
	14	1×10^{-14}	1

TABLE III

Strong Acids and Bases

Acids	
Hydrochloric acid	HCl
Hydrobromic acid	HBr
Hydroiodic acid	HI
Nitric acid	HNO_3
Sulfuric acid	H_2SO_4
Perchloric acid	$HClO_4$
Bases	
Sodium hydroxide	$NaOH$
Potassium hydroxide	KOH
Calcium hydroxide	$Ca(OH)_2$
Magnesium hydroxide	$Mg(OH)_2$

TABLE IV

Properties of some Weak Acids and Bases

Compound	pH of .1M solution
Acids	
Acetic acid	2.87
Boric acid	5.1
Citric acid	2.1
Potassium bitartarate	3.7
Oxalic acid	1.3
Hydrogen peroxide	6.3
Bases	
Ammonia	11.1
Sodium hypochlorite	10.3

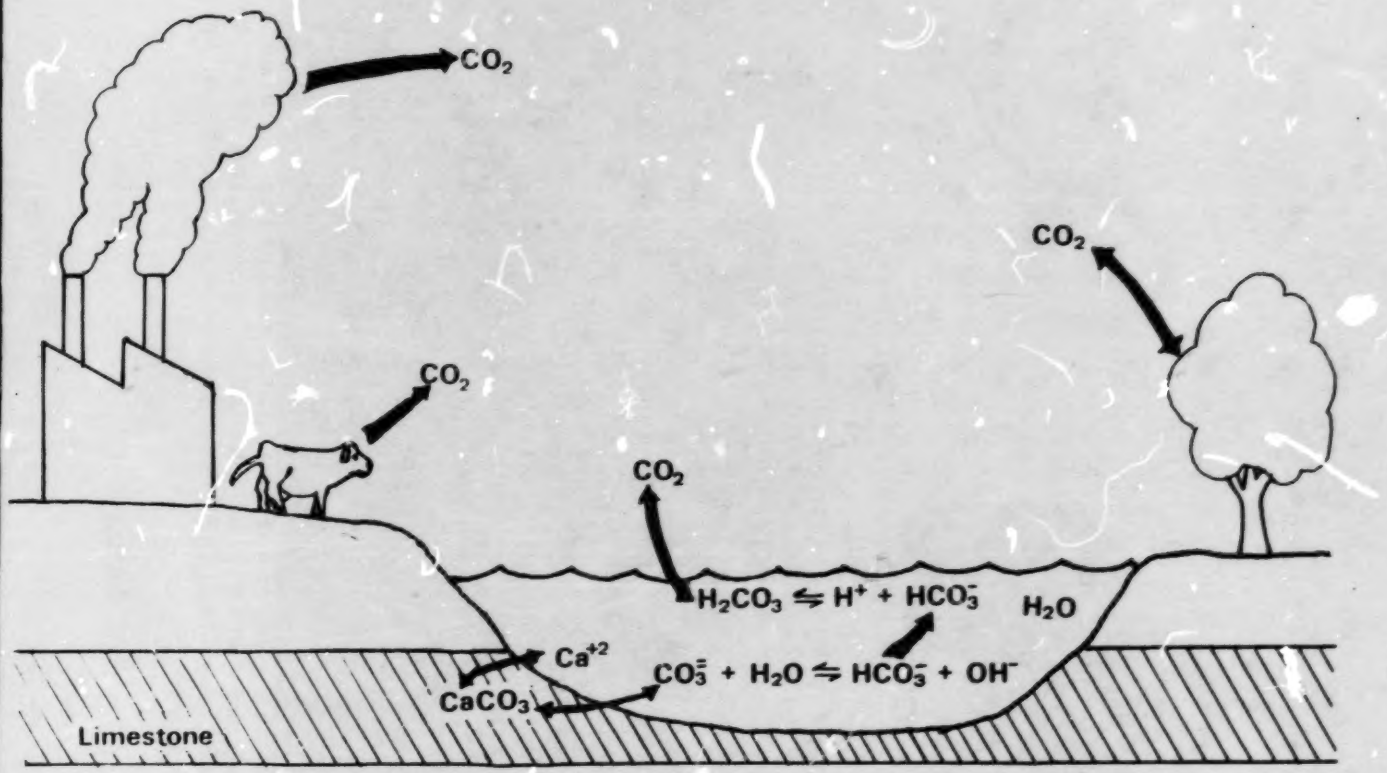


Figure 1. This diagram illustrates the natural carbonate buffer system. The main buffering action comes from the H_2CO_3/HCO_3^- pair. The dissolved CO_2 from the air while the bicarbonate ion comes from dissolved limestone. Sources of atmospheric CO_2 include combustion processes, animal respiration, and decaying organic matter.

Background Information

SOME ASPECTS OF THE CHEMISTRY OF THE ATMOSPHERE

Almost everyone knows that the air we breathe is made up of oxygen, nitrogen and, of course, some water. There are traces of other gases such as argon and carbon dioxide. Beyond these major and minor constituents there is a whole array of trace components that are present only in minute quantities but whose impact on the air and on the general environment is quite large. Of interest to us are those substances that are introduced into the atmosphere in some manner or other. These trace substances include gases, solid [illegible]ols (tiny droplets of liquid) and material dissolved [illegible]tation. A partial list is given in Table I. Appearing [illegible] also are the sources of those components. Scientists sometimes divide the emission into those that are called 'natural' and those that are 'man-made' or anthropogenic. Air contamination from human sources is not a new phenomena. It began with the discovery of fire, but the magnitude of the contamination has increased dramatically since the Industrial Revolution.

Of particular interest to us are the components that find their way into the soils and waters by being removed from the air in some manner. Deposition occurs principally by two methods: precipitation (as rain, snow, sleet or hail) and by what is called dry deposition. 'Dry' deposition comes about from the gravitational settling of particles or aerosols in the air. We are concerned mainly with those substances that are deposited by either wet or dry deposition which in some way affect the acidity of soils and natural waters.

In order to understand how air-borne contaminates affect the acidity of natural systems, we first must know something about what you might call the 'natural' acidity. Water in contact with air will dissolve small quantities of gases in the air. Of all the major and minor components of air, excluding 'contaminants', only one gas has any effect on the pH of water and that is CO_2. In a summary way*, we can indicate the overall process in the following equations:

$$CO_{2(g)} + H_2O \rightleftharpoons H_2CO_3 \qquad 1a$$

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \qquad 1b$$

* See footnote in the "Acid-Base" section, p. 4.

Thus precipitation is expected to be somewhat acidic due to the dissociation of the weak acid, known as carbonic acid. Measurements and calculations show that the pH from dissolved CO_2 is approximately 5.6. In the discussion of acid rain, 5.6 is used as a benchmark against which it is determined whether the precipitation has had its pH shifted significantly from this 'natural' value. You might note an ambiguity here in that while the pH of water in contact with air containing the usual amount of CO_2 is 5.6 any real sample of air, even excluding substances from anthropogenic sources, has traces of acidic chemicals from natural sources. Thus the bench mark does not necessarily represent a value related to the pristine state of nature, rather it establishes a relative value against which to measure shifts in pH.

Of all the substances given in Table I, two have received the most attention in the acid precipitation debate. They are sulfur dioxide, SO_2, and the nitrogen oxides, NO_x (a symbol standing for several oxides of nitrogen including NO, NO_2 and N_2O). As the table shows, the sources for these emissions comes from a variety of places. Natural SO_2 emissions include volcanic origins, and decomposition of organic matter. Anthropogenic emissions come mainly from the combustion of fossil fuels which contain a trace amount of sulfur in them. Also, the smelting of certain metallic ores creates SO_2 emissions. NO_x natural sources include the oxidation of naturally occurring ammonia (NH_3) to NO_x. The ammonia sources come mainly from decomposition of organic matter, as well as the formation of NO_x from atmospheric nitrogen by lightening. Man-made sources are generally the result of combustion processes where the high temperatures involved cause a reaction between atmospheric nitrogen and oxygen to form the oxides of nitrogen. Scientists generally agree that the most important contributor is the internal combustion engine. It is also likely that some NO_x emissions may come from ammonia fertilizers with the oxidation occurring as in the case of natural ammonia sources. Figure 1 summarizes emission sources for these two important air contaminants.

There has been an increase in the amount of SO_2 and NO_x emissions. This change is shown in Figure 2, and it is generally agreed that the cause of this increase is due to an increase in industrial and transportation activity.

Sulfur and Nitrogen Cycles

Both sulfur compounds and nitrogen compounds that are considered contaminants in the atmosphere go through a series of transformations involving sources and sinks for these substances. The sources include natural ones as well as anthropogenic ones. Figures 3 and 4 summarize the general schemes. It should be noted that in the nitrogen case, both HNO_3 and NH_4^+ are acidic though not all the deposition from NO_x will be acidic since some of it will be deposited in the form of nonacidic nitrate salts. In the sulfur instance, deposition is usually by some form of sulfate some of which will be acidic. Certain details of these

cycles will not be examined.

The importance of SO_2 and NO_x to the acid rain problem comes about by the chemical transformation of these substances into compounds which are acidic. SO_2 can react with oxygen in the air to form SO_3. The process proceeds slowly but in the presence of certain trace amounts of chemicals, it can go much faster. SO_3 then dissolves in water to form sulfuric acid, H_2SO_4.

$$SO_2 + \tfrac{1}{2} O_2 \rightleftharpoons SO_3 \qquad 2a$$

$$SO_3 + H_2O \rightleftharpoons H_2SO_4 \qquad 2b$$

Scientists are still not certain exactly how reaction 2a comes about in the atmosphere, and it is very possible that SO_3 is not formed by a direct reaction with O_2 but rather some other substance may provide the extra oxygen. With the nitrogen oxides, conversion of the various forms to NO_2 and then the subsequent reaction to give the strong acid, HNO_3, yields the acidic component. The presence of these two strong acids, HNO_3 and H_2SO_4, is the focal point for the problems associated with acid rain. If they are present, they will shift the pH to more acidic values than the benchmark value of 5.6.

It should be noted that Figures 3 and 4 just indicate the overall transformation processes. The details of how NO_x is transformed into nitric acid are not indicated. There is still much that scientists do not know about these transformation processes, except that simple equations like Equations 2 do not represent the details of the chemistry, only the gross transformations that take place. The rate at which transformations occur may also be a factor in determining what particular chemical reactions are most important. We have already indicated that the direct conversion of SO_2 to SO_3 is too slow to be an important contributing factor; however, the reaction can be speeded up by the presence of certain chemicals called catalysts. It should also be noted that once the transformation of say NO_x to nitric acid has taken place it is very difficult if not impossible to determine the source of the original NO_x and to label it as natural or anthropogenic.

The acid components, HNO_3 and H_2SO_4, come into contact with the ecosystem, as you have read, by two processes, wet or dry deposition. In dry deposition, the acids are attached to dust or aerosol particles which settle to the surface. Wet deposition, where the acids are dissolved in water and come down as precipitation, is by far the better studied and better known process and is the source from which most of the concern about acid rain has come. Measurements of hydrogen ion concentration or pH have been made on precipitation in Sweden and Norway for many years. Data from the United States and Canada are not as complete and, as we will see later, is under some criticism as to its accuracy and

meaning. Figure 5 presents some findings with respect to the acidity of precipitation in the United States and Canada. As can be noted from the diagrams, much of the regions have average precipitation values below the benchmark number of 5.6 pH units.

It has long been known that SO_2 emissions can cause severe local effects not only from the formation of sulfuric acid but also from the corrosive nature of SO_2 itself. This local effect has been documented in London when coal was used for heating as well as in the near vicinity of ore smelters such as the plant at Sudbury, Ontario. Such effects as stunted vegetation, no vegetation, lakes without aquatic life as well as destruction of masonary, limestone structures, and paint have been noted. Of more recent discovery is the concept of long range transportation of air contaminants. Here there appears to be sufficient time for the transformation of SO_2 to H_2SO_4. There is some evidence to suggest that the acid rain that falls on Scandanavia comes from emissions in the industrial regions of continental Europe. They are carried by prevailing winds to Norway and Sweden. It has been suggested that the same type of effect is happening in the United States. The industrial regions of Ohio, Indiana and Illinois may be the source of SO_2 and NO_x which are then transported to the Northeast and into Canada.

The fate of HNO_3 and H_2SO_4 when they are deposited is subject to some uncertainty. Precipitation which soaks into the soil will interact with the very complex chemistry found there. Some soils may be acidified by acid rain, depending on the composition of the soil, particularly if there is an absence of bases to react with the acids and buffer systems in the soil to resist pH changes. In addition to the possibility of acid-base chemistry, there is the chance that the substances will be metabolized by plants. The nitrate ion, in particular, is a plant fertilizer. Acid rain which ends up in lakes or streams either by falling directly into them or by run off will acidify the waters and cause the pH to go down. The extent to which the pH changes is determined by the ability of the natural waters to buffer. The lakes in the Adirondacks have a low buffering capacity compared to other regions because the rocks which are in contact with natural waters are granite-like and low in limestone, the source for $CaCO_3$ in the buffering reaction (see the Acid-Base section). The soil in the Adirondacks is also low in its ability to neutralize acid precipitation because it is derived from the weathering of the granite rocks. Thus there is a double problem, acid rain into the lakes and acid runoff too. The problem of runoff is magnified by what scientists call melt shock. Precipitation in the form of snow usually accumulates during the winter, locking the acids in the snow. In the spring, the melting of the snow happens over a fairly short period of time dumping the winter's accumulation of acid into the lakes. This fairly large amount of acid causes the buffering system to fail and creates a rather large change in the pH. Fish kills have been observed in Norway from this effect.

The effect of dry deposition is much more difficult to access since not much is known about the process. Acidic substances

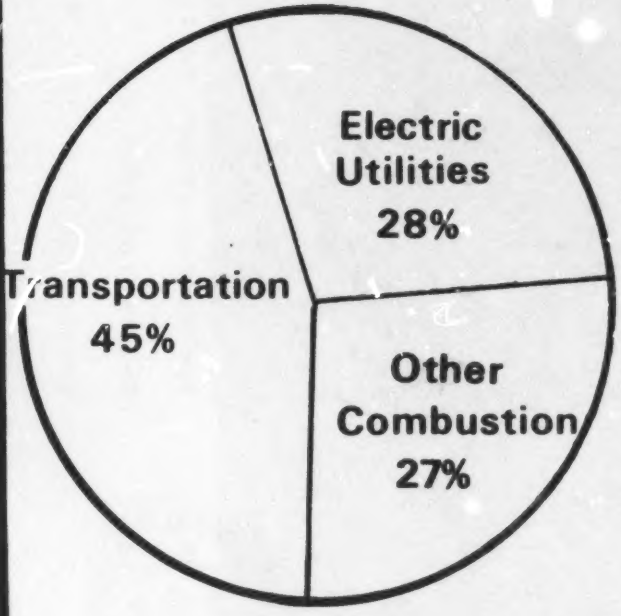
in dry deposition often adhere to very small dust particles and their acidic activity may be modified by the composition of the dust particle. The process of attaching to the surface may also modify the activity of the substance. The nature of the surface upon which dry deposition takes place will also have a role in determining the impact the acidic compounds on the environment. Clearly there is much complex chemistry taking place here. The measurement of dry deposition is also more difficult than determining the acidity of a sample of water. One method for measuring dry deposition relies on an open bucket in which the deposition is collected with the bucket being covered when precipitation occurs to avoid contamination of the solids and aerosols by the precipitation. The collected sample can then be analyzed in various ways.

Much of the cause for concern with the acid rain has been the observed effect that there has been a marked change in the patterns of aquatic life in many lakes in Norway, Sweden, the Adirondacks, and parts of Canada. Many lakes which had fish in them years ago now have none. There has been documentation that the pH values of these lakes has gone down over a period of time.

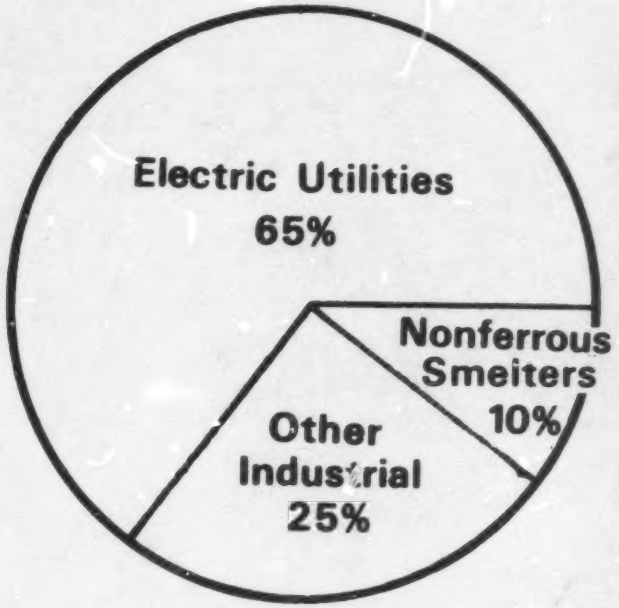
TABLE I

Some Compounds Found at Trace Levels in the Atmosphere

Compound		Sources
Carbon Compounds		
Carbon dioxide	CO_2	Animal and plant repiration, combustion, biological decay
Carbon monoxide	CO	Combustion, atmospheric reactions from methane
Methane	CH_4	Decomposition in marshy areas, natural gas deposits
Sulfur Compounds		
Sulfur dioxide	SO_2	Fossil fuel combustion, smelting, refining, volcanoes
Sulfur trioxide	SO_3	Volcanoes, combustion, conversion of SO_2 and H_2S
Hydrogen sulfide	H_2S	Biological decay, volcanoes, industrial sources
Sulfate ion	$SO_4^=$	Sea spray, conversion of SO_3 and SO_2
Nitrogen Compounds		
Nitrous oxide	N_2O	Bacterial action
Nitric oxide	NO	High temperature combustion (mainly internal combustion engines), lightening, other natural sources
Nitrogen dioxide	NO_2	Combustion processes, lightening, conversion of NO
Ammonia	NH_3	Biological decay, fertilizers
Ammonium ion	NH_4^+	Conversion from NH_3
Nitrate ion	NO_3^-	Conversion from NO_2



SOURCES OF NO_x



SOURCES OF SO_2

Figure 1. U.S. sources of precursors for nitrogen oxides and sulfur oxides on an annual basis from anthropogenic sources.

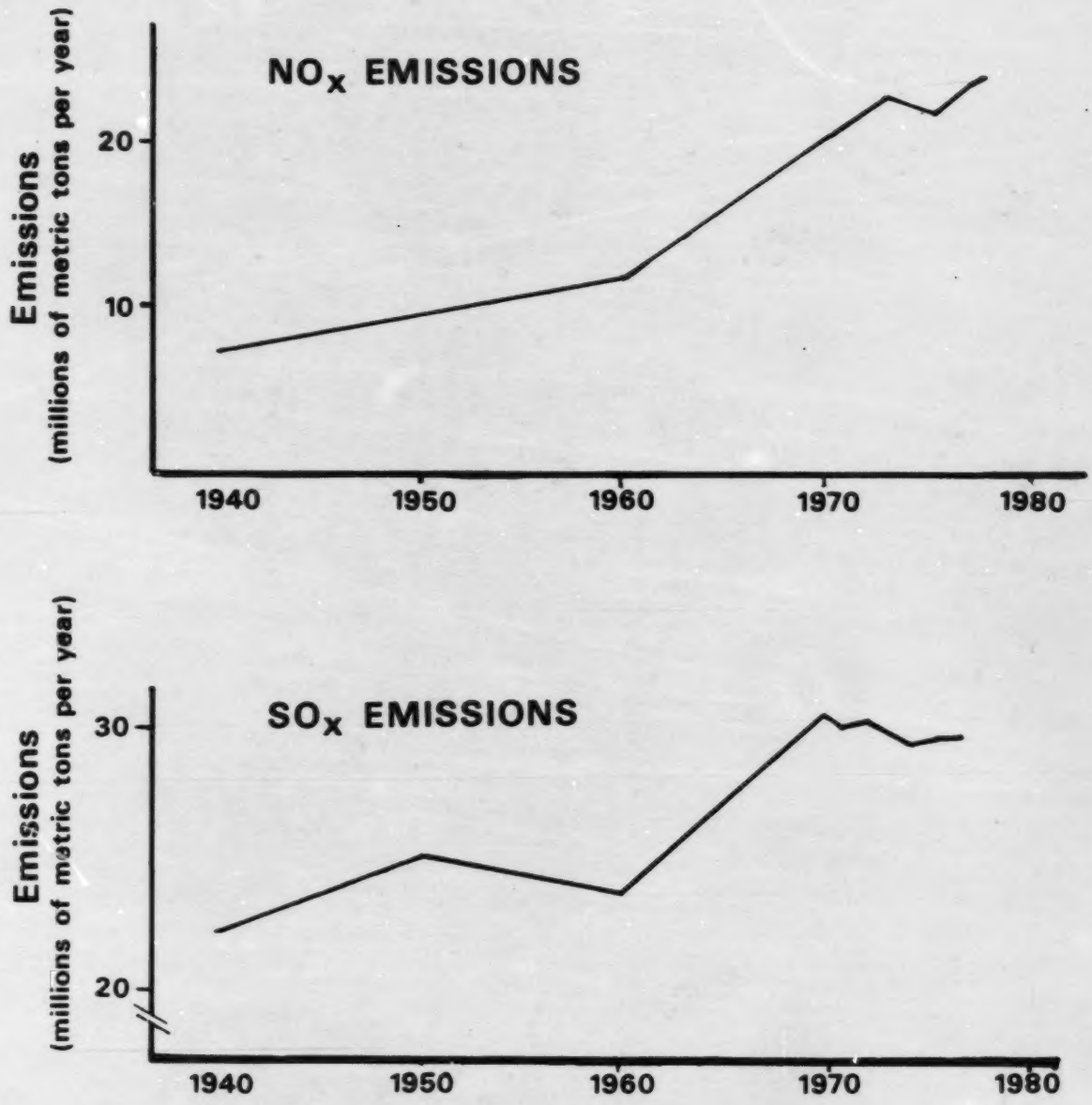


Figure 2. Change in NO_x and SO_2 emission in the U.S. from anthropogenic sources.

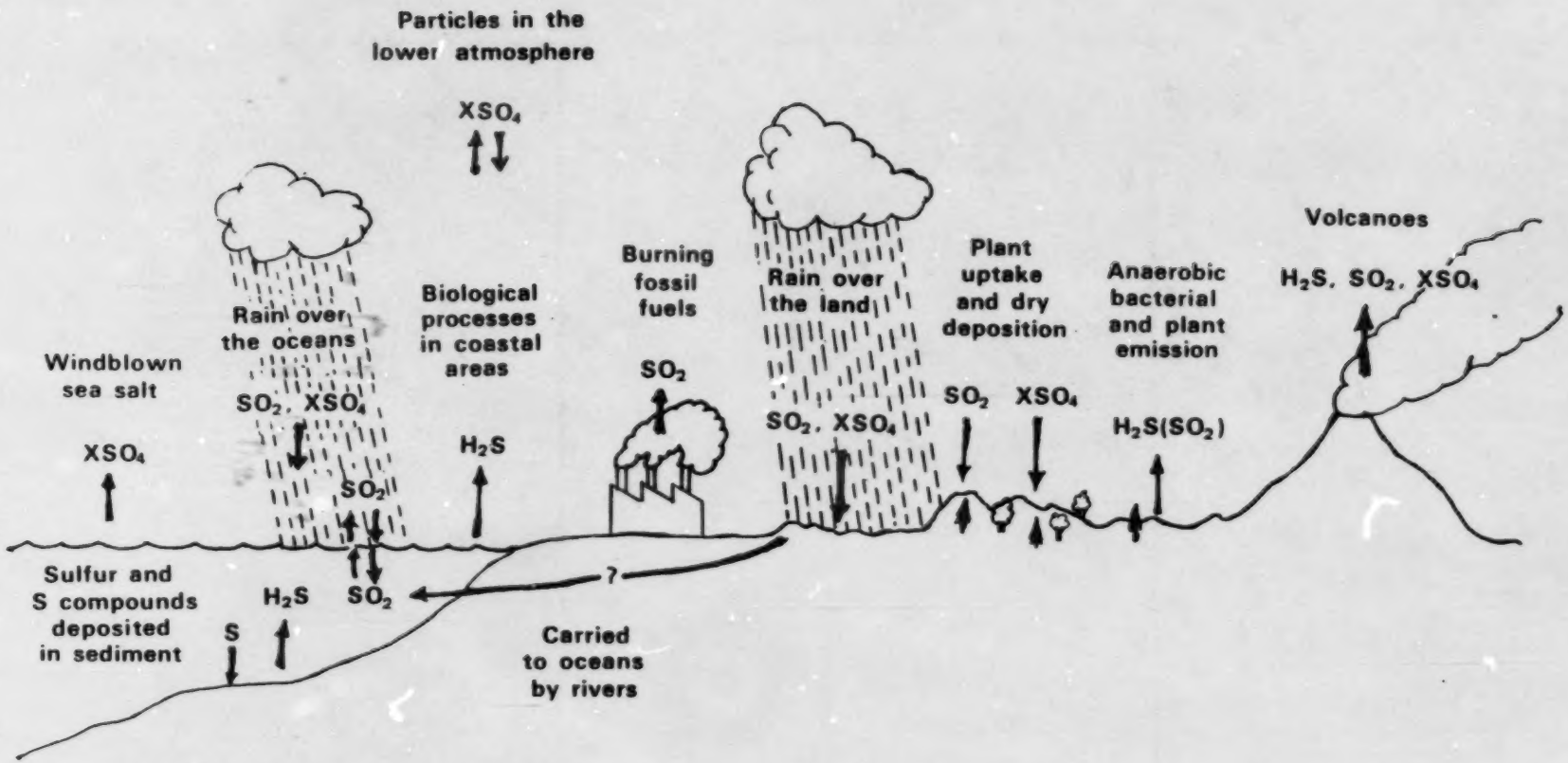


Figure 3. The Sulfur Cycle

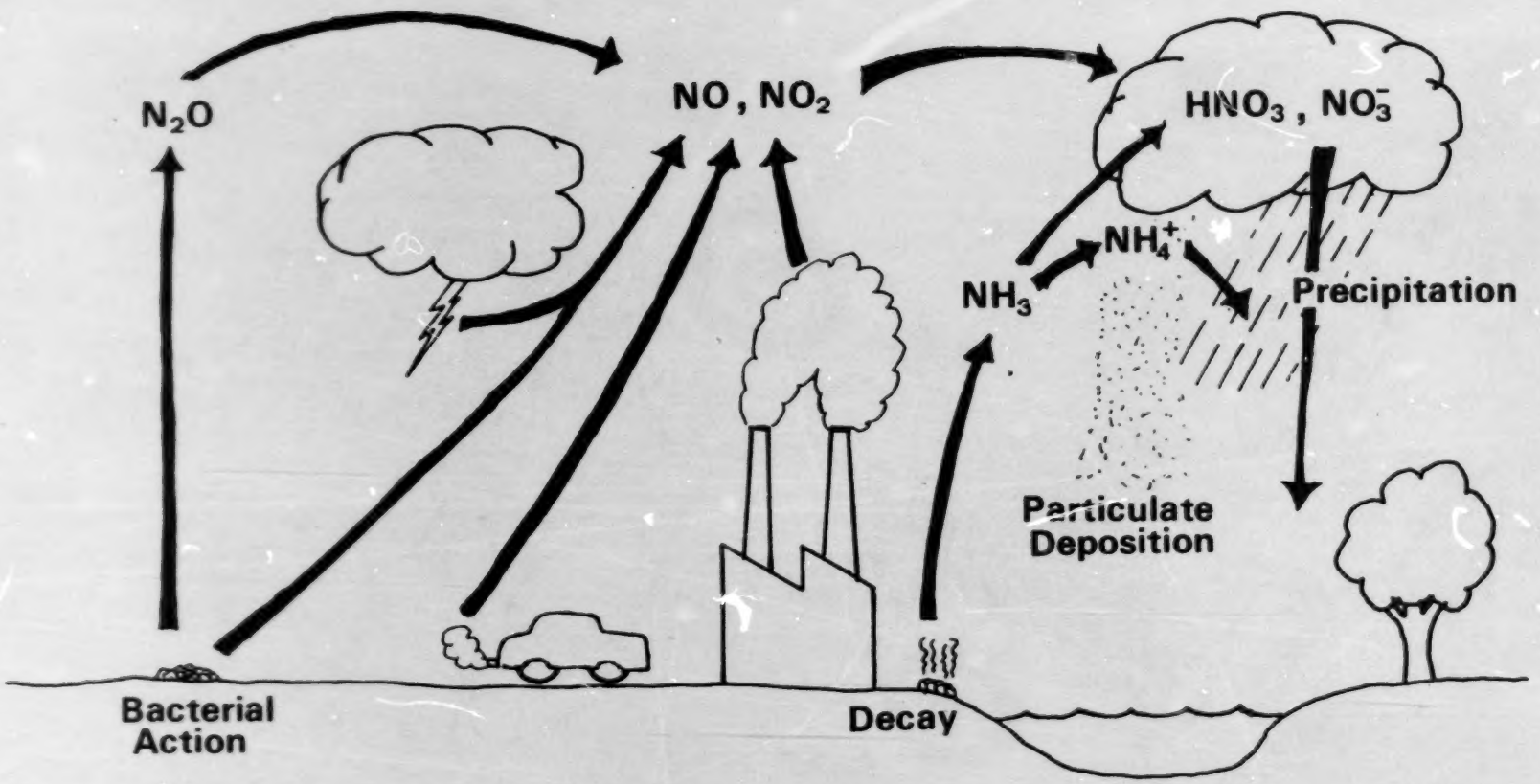


Figure 4. The nitrogen cycle. Emissions from various natural and anthropogenic sources result in the conversion of various nitrogen oxides and ammonia to nitric acid, nitrate ion and ammonium ion. These species are returned to the surface either by precipitation or by dry deposition.

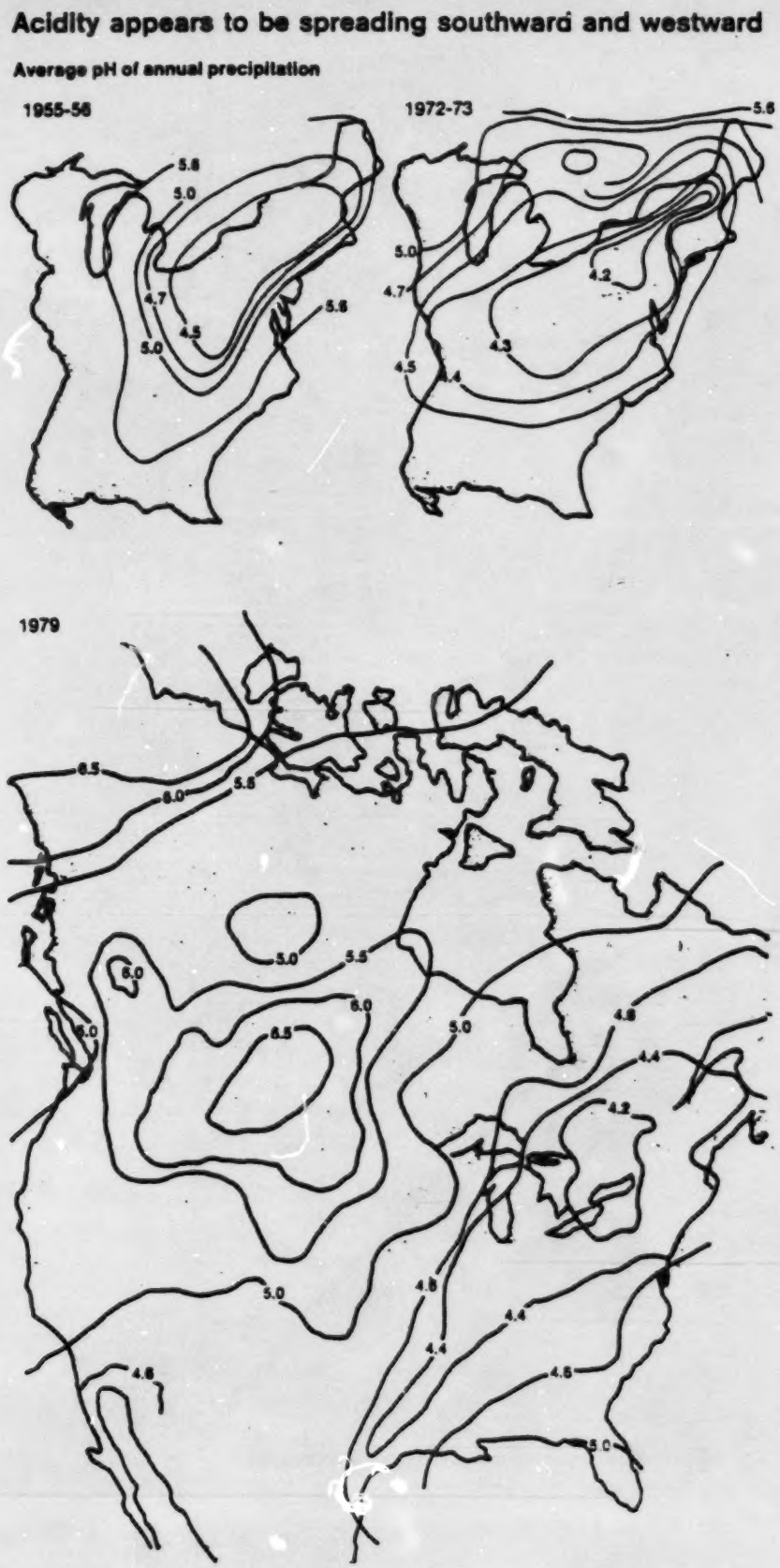


Figure 5. Trends in acid precipitation in the U.S. and Canada.

The Acid Rain Controversy

"Our knowledge of acid rain resembles
swiss cheese - there are a lot of holes,
but some substance." (anonymous)

Here are some examples of what experts have said about acid rain.

A. ---48,000 lakes in North America are doomed to destruction.
---8 billion estimated lost from the American economy.
---thousands of individuals are physically affected - some fatally.
---all because of ACID RAIN.[1] (Atlantic Salmon Foundation)

B. "...there is "overwhelming" circumstantial evidence supporting claims that power plant emissions are a major factor in forming acid rain. ---There is little probability that some factor other than emissions of sulfur and nitrogen oxides is responsible for acid rain."[2]

C. Some of the impressions of increasingly acid rain may well have arisen from comparisons of data obtained by different methods, with the tendencies to detect differences due to the method of analysis rather than the rain itself.

It is premature to state that rainfall is not increasing in acidity anywhere. But <u>not one of the reports of increasing acidity has stood up under scientific challenge</u>.[3]

D. "Without question, acid rain is the most serious and deadly environmental problem that man has ever faced. Acid rain knows no boundaries and its effects are catastrophic."[4]

E. "There is no evidence that acid precipitation is either a major problem or a threat to public health nor is there any scientific consensus pointing to a broad crisis associated with precipitation acidity.[5]

F. Acid precipitation is a non-issue that has been blown out of proper proportion by antigrowth environmental extremists.[6]

The tone of these statements is quite different. Suppose we had a scale from 1-10 with 10 representing the most extreme view (offering the least evidence) and 1 representing something approaching rational criticism. Where would you place each of the quotes? Put letters over numbers.

Exercise 1.

1----------/
1 2 3 4 5 6 7 8 9 10

In making your evaluations you relied on your background knowledge and your innate sense of reasonableness. In a sense you tried to look for reasoned criticism which stands behind those overt disagreements.

There is a world of difference between disagreement and reasoned criticism. When one person asserts an opinion and another denies it, he or she states an opposing position. This is disagreement. Such conflicts are common, and they do occur in science as well as everywhere else. Reasoned criticism, however, is a process of evaluating the evidence which supports a position. Science has developed many procedures for producing evidence, and, of course this is helpful. Unfortunately, the evidence may be inconclusive and require interpretation. Reasoned criticism and rational deliberation, therefore, frequently requires experts and educated laymen to discuss the strengths and weaknesses of various kinds of evidence.

Here we encounter a very important feature of policy debate which occurs in virtually every environmental issue but is seldom publicly stated or openly admitted. One cannot evaluate the scientific information, the evidence, or the facts without introducing or presupposing some preferences or values. For example, the Atlantic Salmon Foundation directly represents the fisherman of Canada's coastal provinces. They will naturally look for evidence which supports their beliefs that acid rain is caused by power plants in the United States and that acid rain is destroying the salmon spawning grounds. By contrast, the Edison Electric Institute represents utility companies in the United States, and it will try to interpret the evidence to support the belief that "there is no evidence pointing to a broad crisis" (quote F above). Both sides can agree on certain facts, others are in dispute, and they disagree over the inferences or interpretations placed upon those facts. If one wants to understand a complicated issue, like the acid rain debate, one must identify the interpretations which are intertwined with the facts. Sometimes there is a clear distinction between facts and values (or

interpretations) but many times there is no sharp distinction. This exercise asks you to use your knowledge of basic chemistry to identify where and how facts are interpreted or evaluated. A person does not have to be an expert in facts in order to become aware of the ways in which those facts are used or twisted.

One way to evaluate evidence is to begin with facts about which both sides agree. Some of this agreement can be explicit, but it can also be shown tacitly, by silence or by partial acknowledgement that an allegation appears credible.

These are some uncontroverted facts:

1. Some coal-burning power plants emit large amounts of sulfur dioxide and nitrogen oxides.

2. Sulfur dioxide and nitrogen oxides react with oxygen and moisture to form sulfuric and nitric acids.

3. Rain is sometimes more acidic than generally expected or accounted for. Available data show that precipitation measured in certain parts of the United States particularly the eastern part of the country, has a pH below 5.6.

4. Available data show that 264 Adirondack lakes are no longer able to support fish because of high acidity. 256 more lakes are approaching the same fate. In sum, in certain lakes the acidification process has begun and appears to be increasing.

These facts say nothing about causes. Did you notice that (1) and (2) talk about power plant emissions while (3) and (4) talk about the condition of rain and lakes? Sometimes the way facts are arranged or organized can make you think there is causal connection between them. Did reading (1) and (2) first make you think they were <u>the</u> causes of acid rain? Scientists working for the utilities maintain that there is merely a correlation or coincidence between emissions and increased acid precipitation. They believe no one has established a direct causal connection; consequently, there may be contributing causes other than emissions which produce acid rain. The fundamental scientific question is do we know enough to say that increased emissions cause acid rain, or must we restrain our judgments to merely indicating a correlation between emissions and pollution?

Environmentalists build their case for acid precipitation on three broad assertions:

---That it results in large part from man-made emissions of oxides of sulfur and nitrogen;

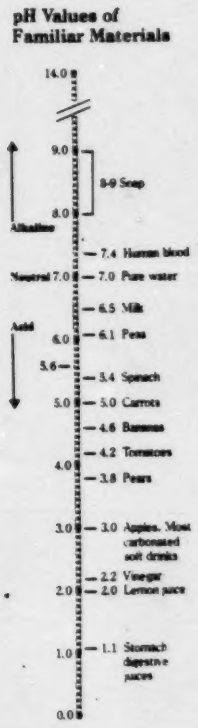
---That these emissions are transformed in the atmosphere to sulfuric and nitric acids, and can be transported great distances; and

---That these acids are then deposited where they harm vegetation, soils, surface water, and materials.

The charges cover three categories, emissions, transformation in atmosphere, and deposition. The Electric Power Research Institute (EPRI), defender of the utilities position, has responded to each charge by pointing to counter evidence.

Let's review EPRI's case.

1. What is the pH scale?



2. What does it measure?

3. The benchmark of "natural rain" is 5.6. Acid precipitation in the range of 4.2-5.0 has been recorded in much of the Eastern United States and Canada. EPRI likes to compare these values to familiar objects. (See chart). Do you think this is misleading? Why or Why not? Is it helpful to think of acid rain as having the same pH as a banana?

4. Although pure water is given a pH value of 7.0, everyone recognizes that naturally occurring rain will not have this value. Why?

An EPRI spokesman maintains that the "natural acidity" of rain water is itself an issue.

> The pH of a pure water droplet in equilibrium with the average carbon dioxide concentration of the atmosphere is 5.65. This value is said to be the "neutral" point of precipitation. Any precipitation with a pH above that value is alkaline and any below is acidic. While this may or may not be a valid reference point, it should not be considered the "background" or "natural" acidity of precipitation. Even without anthropogenic influences, there are natural sources of sulfur oxides, nitrogen oxides, and other species important to determining the

precipitation acidity at any given time. Hence, trying to quantify man's perturbation of the natural condition will never be possible, since the "natural" or "background" condition cannot be known.[7]

5. Do you agree with the conclusion (underlined)? Why or Why not?

EPRI offers other evidence for rejecting the notion that "clean" rain should be designated pH 5.6.

> In the forest areas of Brazil at the headlands of the Amazon River, an area remote from civilization, the monthly average of 100 rain events in the 1960s ranged from pH 4.3 to pH 5.2, with the median value of pH 4.6 and one reading as low as pH 3.6.
>
> The rainfall from two hurricanes in September, 1979 sampled at six stations from Virginia to upstate New York, averaged pH 4.5, with one reading as low as pH 3.6. Much of the weather came directly from the Atlantic Ocean and was quite unlikely to have been affected by emissions from any industrial activity.
>
> On the island of Hawaii, remote from all industrial activity, the weighted average of precipitation over a 4-year period was pH 5.3, with a minimum value of pH 3.8.
>
> The Global Precipitation Network recently reported the following range of readings:
>
> | | |
> |---|---|
> | Indian Ocean | pH 3.98 - 5.26 |
> | Alaska | pH 4.54 - 5.50 |
> | Australia | pH 4.0 - 5.0 |
> | Bermuda | pH 3.5 - 6.0 |
>
> Rainfall in remote regions of the world is clearly often below pH 5.6. While there are exceptional readings below pH 4 and above pH 5, the average values tend to fall in the range of pH 4.5 - 5.5. Thus, it is questionable whether pH 5.6 is realistic for defining "clean rain" or even whether any single value should ever be designated as a reference point.[8]

6. How would you respond to this issue? Why are reference points or benchmarks, like a 5.6 pH for rain, needed in science?

7. Is it possible to measure relative changes in the acidity of rain without knowing the "natural" condition? Explain how this might be done.

8. What are some of the things, i.e., "contributing species" which may increase the acidity of rain? Begin by listing the emissions of power plants.

9. Could lightning be a contributing species? Why? Explain what happens in a lightning storm.

10. In what way does raising the issue of lightning as a source contributing species support the argument the EPRI is using? Is it a valid issue? Is it testable?

Power companies argue that emissions are not the whole story. For example:

> In order to define the relative importance of each source to the problem this emission information must be tied into the other factors that have been discussed above. What must be considered then, is how such things as transport mechanism, transformation processes, and incorporation mechanisms modify the importance of the relationship suggested by the emissions data.[9]

11. Can you put this claim in your own words or use one of your own examples? Do you think it is a significant comment - why?

> For example, the emissions data may suggest that lightning is the major source of gaseous NO_x in the atmosphere and hence imply its importance to precipitation acidity. However, NO_2 solubility theory would suggest that such NO_x, as NO_2, would not be very important. It would need to be somehow converted, relatively quickly, into nitric acid or particulate nitrate to become important. This conversion is not considered likely because of the

relatively short lifetime of clouds. But, as noted earlier, NO_2 retention in precipitation becomes greatest during successive freezings and thawings, a process which is typical in clouds associated with lightning.[10]

12. Why do the power companies want to emphasize chemical processes other than mere emissions data? Is it reasonable to do so?

13. Given your list of possible contributing species, explain by words or equations what sort of transformations might take place in the atmosphere.

14. Why does the question of transformation enormously increase the complexity of determining the causes of acid rain?

Emphasizing the complexity of the issue is a way of undermining the assertion that we know the causes of acid rain. John Jansen, an EPRI scientist, illustrates this strategy.

> In the case of the problem of the acidification of lakes there is increasing evidence that: (1) at the very least, the cause and effect relationship is not as simplistic as much of the recent literature implies, and (2) a number of other activities and processes, both natural and manmade, could contribute to or even be the major cause of lake acidification.
>
> A number of activities may be causing the lakes in Scandinavia and the northeastern United States to acidify. Some are man-made and other are natura. Some of these activities are:
>
> (1) dry deposition of atmospheric pollution, and
> (2) natural lake acidification processes.[11]

When someone says, "The coincidence of A with B is too simplistic," they often want us to infer that the true cause is more complicated, and hence not "too simplistic". This is another way of saying we know correlations but not causation.

15. From what you know about dry deposition and the buffering process explain why further study of (2) and (3) above will be more "complicated" and more difficult to understand than wet deposition?

Now read carefully what Jansen says about dry deposition.

> While it is a very important step to begin to measure a dry deposition and to consider it on equal terms with deposition, there is a major drawback in the NADP. The measurement of dry deposition is by an open plastic bucket, which is covered when it rains. This technique is commonly viewed as worthless. It has no relationship to reality since dry deposition depends strongly on the characteristics of the surface upon which it occurs. At this time, there are no good, routine monitoring techniques for dry deposition available. It is an area which needs intensive research and is just now beginning to get it. However, it must be cautioned that even though little is known in this area, it should not be neglected when considering the effects of total and/or wet deposition. Even gross estimates of its magnitude are useful and always should be a part of any research on the effects of atmospheric deposition on ecosystems.[12]

16. Can you list some reasons why many scientists would consider the "open plastic bucket method" completely worthless?

17. If this method is worthless, why would the author welcome "even gross estimates" as "useful"? (Hint: remember that Jansen is arguing for a more complicated cause which includes dry deposition.)

18. Do you think it is reasonable to accept "worthless data" even if it will help prove your point? Is it misleading to do so?

Obviously, EPRI scientists do not think it is misleading. They believe the problem is very complicated; consequently, they will take any kind of evidence which demonstrates their point. Their values influence what they will accept as fact. One of

these values is the claim that we must investigate all possible situations which could cause acid rain.

> It has been popular to attribute the problem of lake acidification to the purported increase in precipitation acidity because both are supposed to have occurred over the same time period. However, in order to understand why a problem exists and, hence, design effective corrective action, one must explore <u>all possible situations which could cause that problem and determine the relative contribution to the problem from each</u>.[13]

19. Concentrate on the underlined sentence. Do you think it is reasonable to look into, "all possible situations which could cause the problem" before seeking to find ways to solve it?

Clearly the power companies want further investigation. They do not want to be regulated or required to reduce emissions if it is remotely possible that emissions do not contribute substantially to acid rain formation. In a sense there is no "right answer" here. If your interpretation is guided by a belief in investigating all possible contributing causes, you will not act for pollution control until more is known. Good research science is frequently motivated by a desire to know <u>everything</u> about a particular event. Total knowledge is an ideal or supreme value. It says seek knowledge for knowledge's sake, be cautious, avoid error and do not act on insufficient evidence. But there is another sometimes conflicting value or ideal. It says seek truth, seek answers to crucial problems, use knowledge to better the human condition. This mode of thinking often leads to the conclusion that action must be taken based on incomplete knowledge of the problem at hand, particularly if a solution to a problem is economically or environmentally necessary. Good applied science operates on those values. Utilities espouse the former; environmentalists espouse the latter. Both are good attitudes; both are needed in science. Unfortunately, they do not lead in the same direction.

To see how they diverge, read this summary of facts which was prepared by two leading environmentalists in 1981.

<u>Exercise 2</u>.

Circle those points which weaken industry's case, star (*) those which you believe industry has responded to, check (✓) those not in dispute.

Atmospheric Chemistry, Transport, and Deposition

1. Acid precipitation (rain, snow, hail, dew, fog, frost) is occurring in large regions of the eastern USA and Canada, Europe, Japan, and in certain urban and rural areas in the western USA.

2. This widespread occurrence of acid deposition results mainly from man-made emissions of sulfur and nitrogen oxides, which are transformed in the atmosphere to sulfuric and nitric acids and transported over great distances.

3. Acid precipitation is only one special feature of the general phenomenon of atmospheric deposition which includes three major mechanisms that transfer substances from the atmosphere into ecosystems: absorption and adsorption of gases; impaction and gravitational settling of fine aerosols and coarse particles; and precipitation, including both dissolved substances and particles that are removed from the atmosphere.

4. The acidity (or alkalinity) of precipitation is measured in pH units. Carbon dioxide combines with water in the air to form a dilute solution of carbonic acid with a pH of about 5.7. For this reason, acid precipitation is arbitrarily defined as precipitation with a pH of less than 5.7.

5. Tall stacks at power plants and smelters decrease ground level concentrations of SO_2 and NO_x, but increase the geographical area of acid deposition. Removal of alkaline particulate matter from stack emissions also increases the acidity of atmospheric pollutants.

6. Analyses of air-mass movements and chemical transformations in the atmosphere indicate that acid precipitation in one state or region comes from emissions from other states or regions.

7. Major anthropogenic sources of acid rain precursors include combustion of fossil fuels (especially coal and oil), certain industrial processes (especially smelting of ores), internal combustion engines' exhausts, and nitrogen fertilizer.

8. Changes in the acidity of precipitation are reflections of changes in the balance between the major cations and anions in precipitation.

9. In a chemical mass balance sense, it is impossible to distinguish the biological effects of "acid precipitation" (wet deposition) from the biological effects of dry deposition.

10. Some substances, such as ammonium sulfate that themselves are not acidic, can cause the acidification of soils when taken up by plants or modified by soil microorganisms. Thus, the concept of "acidifying precipitation" must be added to the concept of "acid precipitation."

11. The potentially injurious substances in dry and wet deposition include not only acidic substances, but also certain toxic gases and organic substances (notably pesticides) as well as various other inorganic substances or heavy metals.[14]

20. Do you think (2) above represents a statement of fact or an interpretation/conclusion? Explain.

Statements 2. and 6. appear to claim that the source of acid rain can be clearly attributed to man-made causes and that acid rain in one locale can be the result of combustion activity at some distance away. Let's look at the nature of the evidence to support these claims. First the facts that seem relevant will be stated.

A. Studies in the Greenland ice cap have shown that the pH of the water from about 180 years ago was 6 to 7.6. This correlates to an increase in the sulfate ion concentration in the ice cap from 1300 to the present.

B. The presence of sulfate, lead and other chemicals in the remote regions like the Greenland ice cap indicate that long range transport of industrial pollutants is possible.

C. Monitoring of precipitation pH in Europe since the 1950's has shown a decrease in the pH of precipitation in that region since the beginning of the monitoring program.

D. The regions of highly acid precipitation in northern Europe has spread out from the highly industrialized areas of Great Britain and central northern Europe to now include the Scandinavian countries as well as all of northwestern Europe.

E. The decrease in pH of precipitation correlates with an increase of sulfates and nitrates in the precipitation in Europe. Over the same period of time there has been an increase in amount of emissions of nitric and sulfur oxides.

F. Regions of highest acid rain and snow fall are those regions with the highest emissions of sulfur and nitric oxides.

G. The prevalent air flow pattern in northern Europe is from the southwest to the northeast, taking air from the highly

industrialized areas of the United Kingdom and central Europe to the Scandinavian countries.

H. A large number of lakes in Norway and Sweden are now acidic and lack any fish populations. This change has been observed in the past 30 years.

I. In the U.S. and Canada there have been a number of lakes that have turned acidic and now no longer support fish populations.

J. There is some evidence (although it is not nearly as complete as in the European case) to suggest that there might have been a decrease in the pH of precipitation in northeastern U.S. and adjacent regions in Canada.

K. There has been an increase in the emissions of sulfur and nitrogen oxides in the U.S. and Canada.

L. The predominent air flow pattern over the eastern half of the North American continent is from the industrialized regions of the upper Midwest to the northeast.

21. These facts can then be seen to lend support to the claims in statements 2. and 6. While the evidence in the case of acid rain in Scandinavia seems fairly conclusive, there are many problems in the North American case. Is it fair to argue from the Scandinavian case to say that the same thing is happening in North America? What evidence is missing in the North American case to allow the equivalence to be more concrete?

22. Is the environmentalist's position one drawn from rational consideration or is it mainly an emotional conclusion?

23. How might the power companies respond to the argument presented above?

What follows is a statement by Eville Gorham, a leading researcher in the acid rain problem for many years and a concerned environmentalist. It represents a summary of the position in opposition to that of the power companies.

A Call for Action

Researchers still need to learn far more about natural controls on acidity, toxins such as lead and mercury, suspected carcinogens such as benzpyrene, dry deposition that is difficult to measure, and the balance between local fallout and long-distance transport. Much as scientists have investigated how much a given amount of phosphate from detergents or fertilizers damages lakes, they have to determine the damage a given amount of acid deposition causes--and how fast lakes recover after it ceases. Harm to forest growth, which could become extremely serious, must be studied over one or two generations of trees, lasting several decades each. We have to learn more about how acid precipitation brings about change over time, as suggested by the Scandinavian studies. We have to look at whole watersheds, including their chemical cycles, and the life cycles of their plants and animals. There are no quick answers to environmental questions.

In the meantime, the weight of all the evidence indicates that acid deposition is a serious and widespread environmental problem, caused largely by sulfur and nitrogen-oxide pollution. Nearly all of the scientists actively studying the problem agree. The Canadian government regards acid rain as Canada's most critical environmental problem. And President Jimmy Carter's environmental message of 1979 called acid rain "one of the two most serious global environmental problems associated with fossil-fuel combustion." (The other is the "greenhouse effect" that will occur in the next 50 to 100 years as accumulating carbon dioxide, also from fossil-fuel combustion, traps heat in the atmosphere and warms the climate.) I believe --as do the governments of Canada, Norway, Sweden, and West Germany, as well as the governors of six American states, the premiers of five Canadian provinces, the Senate Committee on the Environment, and the U.S.-Canada International Joint Commission--that the evidence of damage from acid rain justifies a major attempt to reduce it.

Industry often argues that we should wait until the evidence is much stronger, but there is ample precedent for action on environmental problems even when the chain of causation is unclear. For example, in 1952, when I was living in London, the Great Smog killed between 2,500 and 4,000 people in a week, three or more times the normal death rate. No one contests that statement, yet the chain of causation still has not been completely worked out--it was certainly far from clear at the time of the incident. Nevertheless, the authorities, acting largely upon circumstantial evidence, made great progress in cleaning up the London air. I doubt that anyone suggests they were wrong

to take this very expensive action or that the regulations they issued ought to be rescinded.

> Governments and industries regularly initiate far-reaching and expensive social and economic programs based on evidence not nearly as convincing as in the case of acid rain, where there is already major ecological and corrosive damage. Environmental programs should not require evidence far greater than is demanded of other initiatives, nor should the burden of proof be on the opponents of pollution. If we wait until the last scintilla of evidence has been gathered and the entire chain of causation is proved, a fragile part of life on our planet will have been damaged. Even if appropriate legislation were enacted today, it would probably take from five to ten years to affect emissions significantly.[15]

A slightly different way of saying the same thing comes in a quote from a report by the Subcommittee on Acid Rain from the Fisheries and Forestry Committee of the Canadian government.

> There is clearly an urgent need to generate more scientific evidence on all aspects of the acid rain problem, including emission sources, atmospheric transport of pollutants, atmospheric chemical reactions and specific environmental effects. There is, however, a persistent danger that this legitimate need could be subverted into a substitute for the difficult decisions that ultimately will have to be taken. A substantial body of respected scientific opinion already supports that conclusion that the best available technologies should be implemented as quickly as possible to control emissions at source.[16]

24. How would these spokesmen respond to the claim that we investigate all possible situations which could cause acid rain before taking action?

25. Do you think it is fair to appeal to past circumstances (i.e. London smog control) in order to justify a course of action today?

26. How does this argument differ from that of EPRI spokesman as given on page 7 or on page 9?

Exercise 3.

In this exercise we have not answered the question of who is right about "acid rain". There are many facts which we have not investigated at all, however, you have learned something about how scientists argue when they want to influence public policy. Assume that you must make a brief report to your congressman telling him about your study. The congressman will, in a few days, be listening to testimony from both sides of the debate. In your report tell him what he should expect from both sides, tell him what kinds of misleading statements he might find, and conclude by summarizing your position on the acid rain issue.

Notes

[1]Reported in Comptroller General of the United States, The Debate over Acid Rain--Opposing Views--Status of Research. U.S. General Accounting Office EMD-81-131-1981

[2]Committee on the Atmosphere and the Biosphere, Atmosphere-Biosphere Interactions: Toward a Better Understanding of the Ecological Consequence of Fossil Fue Combustion (National Academy Press 1981)

[3]Katzenstein, A. W. An Updated Perspective on Acid Rain Edison Electric Institute, 1981

[4]Opt. Cit. The Debate over Acid Rain

[5]Before the Rainbow--What We Know About Acid Rain, Edison Electric Institute, 1980

[6]Ibid.

[7]John J. Jansen, Acid Precipitation--A Review of the Issue and Its Uncertainties - Research and Development Department of Souther Company Services, Birmingham AL, p. 9

[8]Opt. Cit. An updated Perspective on Acid Rain, p. 12, 13

[9]Opt. Cit. Jansen p. 10

[10]Ibid. p. 10

[11]Ibid. p. 2

[12]Ibid. p. 4

[13]Ibid. p 4 Emphasis added.

[14]E. B. Cowling and R. A. Lindthurst, "Acid Precipitation Phenomena" BioScience. Vol. 31, No. 19 Oct. 1981

[15]Eville Gorham, "What to do about Acid Rain" in Technology Review. Oct. 1981, p. 59-66 (reprinted with permission of the publishers and author)

[16]Subcommittee on Acid Rain, Still Waters, The Chilling Reality of Acid Rain, Minister of Supply and services, Canada, 1981